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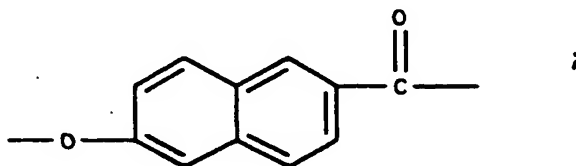
(54) **Melt processable poly(ester-amide) capable of forming an anisotropic melt.**

(57) A melt processable poly(ester-amide) which is capable of forming an anisotropic melt phase is provided. A poly(ester-amide) of the present invention may have recurring units of: (a) 4-hydroxybenzoyl moiety, (b) 6-oxy-2-naphthoyl moiety, (c) 4,4'-biphenol moiety, (d) terephthaloyl moiety, and (e) an aromatic moiety capable of forming an amide linkage in the proportions indicated. Preferably, the moiety capable of forming an amide linkage is derived from p-aminophenol, p-phenylenediamine, N-acetyl-p-aminophenol, etc. The resulting poly(ester-amide) is capable of undergoing melt-processing in the temperature range of from about 300° to about 400° C.

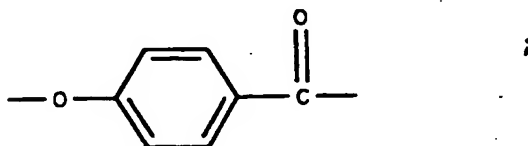
EP 0 513 545 A2

A melt processable poly(ester-amide) capable of forming an anisotropic melt phase at a temperature below approximately 400° C is provided. The poly(ester-amide) of the present invention contains recurring moieties I, II, III, IV, and V wherein:

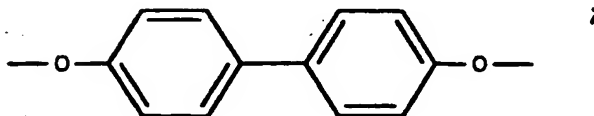
I is



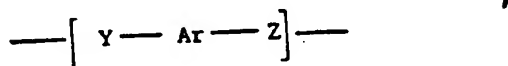
II is



III is



IV is



wherein Ar is a divalent moiety containing at least one aromatic ring, Y & Z are divalent organic or inorganic radicals and may be the same or different and include at least one member selected from the group consisting of NH or NR where R is a 1-6 carbon containing alkyl moiety or an aryl moiety; and V is the residue of an aromatic diol precursor.

Generally speaking, the poly(ester-amide) of the present invention contains from about 1 to about 15 mole percent of moiety I, from about 20 to about 70 mole percent moiety II, from about 5 to about 40 mole percent of moiety III, from about 1 to about 20 mole percent of moiety IV, and from about 5 to about 40 mole percent of moiety V.

Typically, the compositions contain from about 2.5 to about 10 mole percent moiety I, 20 to 70 mole percent moiety II, 5 to 25 mole percent moiety III, 2.5 to 15 percent moiety IV, and 2.5 to 15 percent of moiety V. A preferred composition contains about 2.5 to 7.5 mole percent moiety I, at least 50 mole percent of moiety II, from about 5 to about 20 percent of moiety III, from about 2.5 to 10 mole percent of moiety IV, and about 15 to 25 mole percent of moiety V.

A preferred moiety IV is

To a 2 litre "Slim Jim" flask equipped with a C-shaped 316 stainless steel, gas inlet tube, thermocouple, a Vigreux column attached to a condenser and receiver were added the following:

- (a) 496.8 grams of 4-hydroxybenzoic acid (3.6 moles);
- (b) 56.4 grams of 6-hydroxy-2-naphthoic acid (0.3 moles);
- 5 (c) 139.5 grams of 4,4'-biphenol (0.75 moles);
- (d) 174.3 grams of terephthalic acid (1.05 moles);
- (e) 45.3 grams of N-acetyl-p-aminophenol (0.3 moles); the flask was immersed in a sand bath and provided with means to accurately control the temperature. The flask was thoroughly purged of oxygen by evacuation and flushed with nitrogen three times, and slowly heated in the sand bath; and
- 10 (f) 10 mls. of a 1.2% (w/v) solution of potassium acetate in acetic acid (60 ppm K^+) were added as a catalyst along with 598.8 grams of acetic anhydride (2.5 % excess). Acetic acid began to distill over and was collected in a graduated cylinder.

The contents of the flask were heated while stirring at a rate of 75 rpm (torque = 13 mV) to 152° C. over a period of 111 minutes at which time 100 mls. of acetic acid had been collected. The polymerization
 15 temperature was then gradually raised to 350° C. over a period of 215 minutes at which time a total of 660 mls. of acetic acid had been collected. The flask was evacuated to a pressure of less than 1.0 mm at 350° C. while stirring. The polymer was stirred at 350° C. until the desired Δ torque was achieved (i.e., Δ torque = 50 mV for this example). During this period the polymer melt continued to increase in viscosity while the remaining acetic acid was removed from the flask.

20 The resulting poly(ester-amide) had an inherent viscosity (I.V.) of 9.1 dl/g as determined in a pentafluorophenol solution of 0.1 percent by weight concentration at 60° C., and a melt viscosity (M.V.) of 581 poise at a shear rate of 10^3 sec^{-1} measured at 345° C in a capillary rheometer using an orifice of 0.015 inch diameter and 1.0" length.

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$$I.V. = \ln(\eta_{rel})/c$$

where c = concentration of solution (0.1 percent by weight), and η_{rel} = relative viscosity. The relative viscosity was measured by dividing the flow time in a capillary viscometer of the polymer solution by the flow time for the pure solvent. When the polymer was subject to differential scanning calorimetry
 30 (20° C./min. heating rate), it exhibited a melt endotherm (T_m) peak at 343° C. The polymer melt was optically anisotropic.

EXAMPLE II - X

35 In accordance with the foregoing example I, nine additional compositions were prepared having different proportions of the five ingredients noted hereinabove. Composition, melting point, I.V. and M.V. for the inventive compositions appear in Table I below. Unless otherwise indicated, properties were measured as in Example I.

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- * measured at 345 °C;
- ** measured at 340 °C;
- * measured at 360 °C
- ** measured at 365 °C

This example illustrates the preparation of a polyester from a 7 mole reaction mixture of 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 4,4'-biphenol, and terephthalic acid in the ratio 60.0:3.5:18.25:18.25 (3.5 mole % HNA and 0.0 mole % APAP). The procedure of Example I was substantially repeated with the exception that the following components were charged into the flask:

- (a) 579.6 grams of 4-hydroxybenzoic acid (4.2 moles);
(b) 46.1 grams of 6-hydroxy-2-naphthoic acid (0.24 moles);
(c) 237.6 grams of 4,4'-biphenol (1.28 moles);
(d) 212.1 grams of terephthalic acid (1.28 moles); and
(e) 10 mls. of a 1.2% (w/v) solution of potassium acetate in acetic acid (60 ppm K^+) were added as a catalyst along with 598.8 grams of acetic anhydride (2.5 % excess); the desired Δ torque was 50 mV, and the reaction temperature was 355° C.

The resulting wholly aromatic polymer had an I.V. of 9.2 dl/g as determined in pentafluorophenol at 60° C., and an M.V. of 492 poise at a shear rate of 10^3 sec^{-1} measured at 365° C in a capillary rheometer. When the polymer was subjected to DSC, it exhibited a T_m of 376° C.

This example illustrates the preparation of a poly(ester amide) from a 6 mol reaction mixture of 4-hydroxybenzoic acid, isophthalic acid, terephthalic acid, 4,4'-biphenol, and N-acetyl-p-aminophenol in the ratio of 50.0:12.5:12.5:20.0:5.0.

- The following components were charged into the flask:

- a) 3.0 mole (414.0 g) 4-hydroxybenzoic acid;
b) 0.75 mole (124.5 g) isophthalic acid;
c) 0.75 mole (124.5 g) terephthalic acid;
d) 1.2 mole (223.2 g) 4,4'-biphenol;
e) 0.3 mole (45.3 g) N-acetyl-p-aminophenol: and

f) 10 ml of a 1.2 (w/v) solution of potassium acetate in acetic acid (60 ppm K^+) were added as a catalyst along with 600 ml acetic anhydride (2.5% excess) and heated to 350°C. The resulting wholly aromatic polymer had an I.V. of 3.6 dl/g as determined in

pentafluorophenol at 60°C, and an M.V. in the range of about 500-700 poise at a shear rate of 10^3 sec^{-1} measured at 340°C in a capillary rheometer. When the polymer was subject to DSC, it exhibited a T_m of 281°C.

5 FIBER PROPERTIES

Fibers were prepared from the compositions of Examples IV, V, and Comparative Example A. The fibers were heat-treated for eight hours in a nitrogen atmosphere at 300°C in an oven. Tenacity, elongation and modulus were defined in accordance with ASTM D 3822-90 and reported in Table II, below, along with corresponding data for Comparative Example B wherein the heat treatment was in stepwise fashion, 2 hours at 230°C, followed by 16 hours at 270°C. Examples IV, V, A are approximately 5 denier. The polymer of Example B was difficult to spin; unable to achieve 5 denier fiber, but 8.5 denier fiber was made.

TABLE II

FIBER PROPERTIES AFTER HEAT TREATMENT*			
POLYMER OF EXAMPLE	TENACITY g/d	MODULUS g/d	ELONGATION %
IV	29.2	1040	2.5
V	31.9	1060	2.7
A	21-22	910	2.2-2.3
B	16	475	3.0

* Single Filament

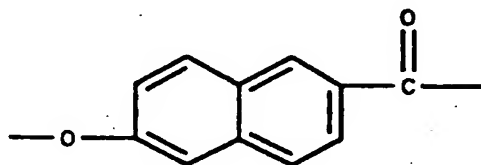
As may be seen from Table II, compositions in accordance with the present invention exhibit both higher modulus and tenacity than other liquid crystalline polymers. This surprising and highly useful characteristic makes such compounds particularly suitable for high performance applications.

While the present invention has been described hereinabove in connection with numerous examples, various modifications will be apparent to those of skill in the art. Such modifications are within the spirit and scope of the present invention, which is limited and defined only by the appended claims.

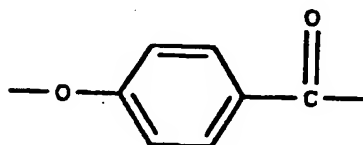
35 Claims

1. A melt processable poly(ester-amide) capable of forming an anisotropic melt phase at a temperature below about 400°C. having recurring moieties I, II, III, IV and V wherein:

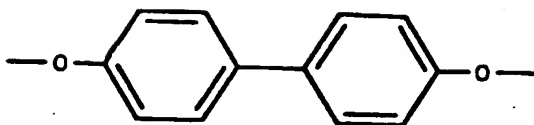
I is



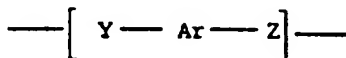
II is



III is



IV is



wherein Ar is a divalent moiety containing at least one aromatic ring, Y and Z are divalent organic or inorganic radicals and may be the same or different and include at least one member selected from the group consisting of NH or NR where R is a 1-6 carbon containing alkyl moiety or an aryl moiety; and V is the residue of an aromatic diol precursor; and wherein said poly(ester-amide) contains from about 1 to about 15 mole per cent of moiety I, from about 20 to about 70 mole percent moiety II, from about 5 to about 40 mole percent of moiety III, from about 1 to about 20 mole per cent of moiety IV, and from about 5 to about 40 mole per cent of moiety V.

2. The poly(ester-amide) according to claim 1 wherein moiety IV is



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3. The poly(ester-amide) according to claim 2 wherein moiety IV is derived from p-aminophenol or N-acetyl-p-aminophenol.

4. The polyester according to claim 3 wherein moiety IV is derived from N-acetyl-p-aminophenol.

5. The poly(ester-amide) according to claim 1, wherein moiety V is a terephthaloyl moiety.

6. The poly(ester-amide) according to claim 1 wherein moiety V is selected from the group consisting of isophthaloyl, terephthaloyl or mixtures thereof.

7. The melt-processable poly(ester-amide) according to claim 1 which is capable of forming an anisotropic melt phase at a temperature of about 350 °C.

8. The melt-processable poly(ester-amide) according to claim 1 which is capable of undergoing melt-processing in the temperature range of from about 300 °C. to about 400 °C.

9. A melt-processable poly(ester-amide) according to claim 1 wherein the aromatic rings of moieties I, II, III, IV, and V are substantially free of ring substitution.

10. A fiber which has been melt spun from the poly(ester-amide) according to claim 1.

11. An injection molded article comprising the melt processable poly(ester-amide) according to claim 1.

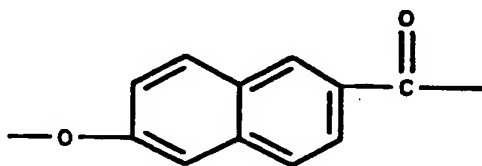
12. A shaped article consisting essentially of the poly(ester-amide) according to claim 1.

13. A melt processable poly (ester-amide) according to claim 1 which exhibits an inherent viscosity in the range of about 1.0 to 12.0 dl/g when dissolved in a concentration of 0.1 percent by weight in

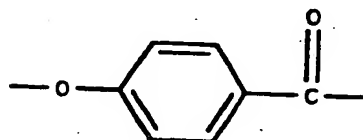
pentafluorophenol at 60°C.

14. A melt processable poly(ester-amide) according to claim 1 which exhibits a melt viscosity in the range of from about 50 to 1500 poise at a shear rate of 10^3 sec^{-1} measured at 365°C in a capillary rheometer.
15. A melt processable poly(ester-amide) capable of forming an anisotropic melt phase at a temperature below approximately 400°C consisting essentially of recurring moieties I, II, III, IV and V wherein:

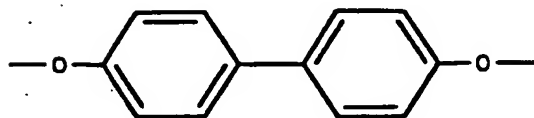
I is



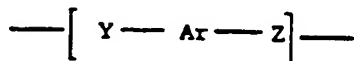
II is



III is



IV is



wherein Ar is a divalent moiety containing at least one aromatic ring, Y & Z are divalent organic or inorganic radicals and may be the same or different and include at least one member selected from the group consisting of NH or NR where R is a 1-6 carbon containing alkyl moiety or an aryl moiety; and

V is the residue of an aromatic di-oyl precursor or mixtures of terephthaloyl with other aromatic di-oyls; and wherein moiety I is present in amounts of from about 2.5 to about 10 mole per cent, moiety II is present in amounts from about 20 to about 70 mole per cent, moiety III is present in amounts of from about 5 to about 25 mole per cent, moiety IV is present in amounts of from about 2.5 to about 15 mole per cent, and moiety V is present in amounts of from about 10 to about 25 mole per cent.

16. The melt-processable poly(ester-amide) according to claim 15, wherein moiety V consists of tereph-

